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X.

ON PENTAMIDOBENZOL.

By A. W. Palmer and C. Loring Jackson.

Presented February 13, 1889.

Nearly two years ago, in a paper upon Tribromtrinitrobenzol,* one of us in conjunction with J. F. Wing described some attempts to reduce triamidotrinitrobenzol, and announced that the work would be continued. Before doing this, however, it seemed advisable to try similar experiments with the triamidodinitrobenzol, as this substance can be obtained much more easily, and the experience gained in this way would be useful when we returned to the much less accessible trinitro compound. Accordingly, we have undertaken together the work on the dinitro compound, which has led, as we had hoped, to the preparation of the chloride of pentamidobenzol; but, shortly after we had sent to the *Berichte der deutschen chemischen Gesellschaft* a preliminary notice† of this substance, a number of the same journal reached us containing a paper by Andrew Barr‡ in which the chloride of pentamidobenzol was also described, and, as this paper, although it came into our hands after our preliminary notice had been sent, was presented to the German Chemical Society a fortnight before ours was written, we have dropped this line of work in order to avoid interfering with Barr, or Merz, in whose laboratory the research of Barr was carried on, and publish in this paper the results which had been already obtained by us when we received Barr's paper.§ The method of making pentamidobenzol used by us is different from that of Barr, who prepared the diamidotrinitrobenzol from the ethylether of trinitroresorcine and alcoholic ammonia, and then reduced this product with tin and hydrochloric acid, whereas we submitted to a similar reduction the triamidodinitrobenzol made by the action of alcoholic ammonia on tribromdinitrobenzol. Both this triamido and the corresponding trianilido compound are new, and an account of them is therefore included in this paper.

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* These Proceedings, Vol. XXIII. p. 138.

† Ber. d. ch. G., 1888, p. 1706.

‡ Ber. d. ch. G., 1888, p. 1541.

§ The publication of this paper has been delayed until the present time, because the change of residence of one of us prevented us from finishing more promptly the study of trianilidodinitrobenzol, a substance which does not come into Barr's field of work.

Triamidodinitrobenzol, $C_6H(NH_2)_3(NO_2)_2$.

This substance was prepared by treating tribromdinitrobenzol,* melting point 192°, with alcoholic ammonia; but this action takes place much less easily than in the case of the corresponding trinitro compound, for whereas that was attacked by alcoholic ammonia in the cold, and the reaction was rendered complete by short boiling in a flask with a return condenser, the dinitro compound gave no action with alcoholic ammonia in open vessels, but it was necessary to heat the two substances under pressure in the water bath to bring about the reaction.

As we had no digester fit for this purpose, we were obliged to heat the mixture in soda-water bottles, which were kept in a boiling water bath for about eight hours. The contents of the bottles at the end of this time consisted principally of a mixture of dark reddish yellow needles with nearly black amorphous masses. There was also a colored alcoholic solution, which on evaporation left a red amorphous substance with a comparatively low melting point; but this was formed in such small quantities that we did not attempt to study it beyond ascertaining the fact that it is not altered by further heating with alcoholic ammonia. The tribromtrinitrobenzol, when treated with alcoholic ammonia, forms a similar by-product,† soluble in alcohol, which is now under investigation. The two products of the reaction which were not dissolved in the alcohol were separated mechanically, washed thoroughly with various solvents, and analyzed without further purification, as they both showed such a slight solubility in all the common solvents that a crystallization of them in any quantity was a matter of very great difficulty. In spite of the great difference in their appearance they both had the same composition, that of the expected triamidodinitrobenzol, as is shown by the following analytical data, in which Analyses I. and II. were made with the reddish yellow needles, Analysis III. with the black amorphous body.

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* The tribrombenzol used in making this substance must be purified by crystallization from alcohol after it has been distilled, as, if this crystallization is omitted, a substance melting in the neighborhood of 95° remains mixed with the tribrombenzol, and gives rise to very impure products after the treatment with nitric acid. The nature of this impurity will be considered in another paper.

† These Proceedings, Vol. XXIII. p. 145.

I. 0.3000 grm. of the substance crystallized in yellow needles gave on combustion 0.3710 grm. of carbonic dioxide and 0.1085 grm. of water.

II. 0.1510 grm. of the crystalline substance like that used in I. gave 42.4 c.c. of nitrogen at a temperature of 8°.6 and a pressure of 748.5 mm.

III. 0.3028 grm. of the substance deposited in black amorphous masses gave on combustion 0.3778 grm. of carbonic dioxide and 0.0925 grm. of water.

	Calculated for $C_6H(NH_2)_3(NO_2)_2$.	Found.		
		I.	II.	III.
Carbon	33.80	33.73		34.02
Hydrogen	3.28	4.02		3.39
Nitrogen	32.87		33.31	

Properties. — The triamidodinitrobenzol, as deposited by the action of alcoholic ammonia on tribromdinitrobenzol, forms either reddish yellow needles, or nearly black amorphous masses. When the substance is crystallized from a mixture of chloroform and alcohol, which can be done only with great difficulty on account of its slight solubility, it forms microscopic yellow plates, or broad flattened prisms, and, if the treatment with the mixed solvents is carried on in a continuous extracter, these crystals collect into characteristic yellow masses shaped like an **S** or **U**. It does not melt even above 300°, but is decomposed if heated more intensely. It is very slightly soluble in alcohol or chloroform, although it imparts a perceptible yellow color to these solvents, more soluble in nitrobenzol, but cannot be obtained in crystals easily from this solution, so that a mixture of alcohol and chloroform is the best solvent for it. In the other common solvents it is either entirely insoluble or very slightly soluble. In this respect it resembles the corresponding trinitro compound, but it is, if there is any difference, slightly more soluble than that. The substance does not form definite salts, although it dissolves easily in concentrated hydrochloric acid forming a dark red liquid. It shows therefore a greater tendency to form salts than the triamidotrinitrobenzol, which is insoluble in strong hydrochloric acid.

Trichloride of Pentamidobenzol, $C_6H(NH_2)_2(NH_3Cl)_3$.

To prepare this substance, some of the triamidodinitrobenzol (either the crystalline or amorphous) was heated on the water bath in a flask with strong hydrochloric acid, a very strong solution of stannous chloride, granulated tin, and some pieces of platinum foil. After some hours the very deep red solution had lost most of its color, but still showed a dirty brownish yellow tint; it was then allowed to cool, when crystals were deposited, which increased in quantity, if the liquid was saturated with hydrochloric acid gas. The crystals were filtered out, and washed with concentrated hydrochloric acid, then, as we did not succeed in removing the salts of tin completely by precipitation from an aqueous solution with hydrochloric acid gas,* the substance was dissolved in very little water and the solution saturated with sulphuretted hydrogen, the stannic sulphide formed was filtered out, and the filtrate, after freeing it from sulphuretted hydrogen with a stream of air, once more saturated with hydrochloric acid gas, which threw down the substance in an essentially pure state and nearly white. In all this work care must be taken to avoid heating the solutions, as the chloride of pentamidobenzol, after the reducing agents have been removed, is easily decomposed by heat into a black tar; the solutions, therefore, should never be concentrated by evaporation on the water bath. We obtained a less pure substance also, if the solution in water and precipitation with hydrochloric acid gas was repeated more than once. The crystals were dried at first in a desiccator over calcic oxide, calcic chloride, and potassic hydrate, and finally heated to 70°–80° for about five hours in an air bath. On analysis they gave the following results.

I. 0.2372 grm. of the substance gave on combustion 0.2445 grm. of carbonic dioxide and 0.1157 grm. of water.

II. 0.1827 grm. of the substance gave 0.1880 grm. of carbonic dioxide and 0.0880 grm. of water.

III. 0.1533 grm. of the substance gave 35.8 c.c. of nitrogen at a tempernature of 14°.2 and a pressure of 750 mm.

IV. 0.1457 grm. of the substance gave according to the method of Carius 0.2377 grm. of argentic chloride.

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* Barr succeeded in removing all the tin from his preparation in this way.

	Calculated for	Found.			
	$C_6H(NH_2)_2(NH_3Cl)_3$.	I.	II.	III.	IV.
Carbon	27.43	28.11	28.06		
Hydrogen	5.33	5.42	5.35		
Nitrogen	26.67			27.08	
Chlorine	40.58				40.33

Considering the ease with which the substance is decomposed, the agreement between these results and those calculated from the formula is as close as can be expected. The method of purification described above, however, does not always give such satisfactory results. Samples from two other preparations gave numbers which differed by about one per cent from those corresponding to the formula, the chlorine being too low and the other constituents too high by this amount; but we ascribe this to partial decomposition of the substance during the purification, as both of these specimens were much darker in color than that which gave the more satisfactory analyses. The objection which might be founded on these results, that our substance was not a definite compound, but a mixture of ammonic chloride with some organic body less rich in nitrogen than the chloride of pentamidobenzol, is removed by the microscopic examination of the substance, which showed that it consisted of well developed rhombic crystals without any admixture whatever, to which may be added the fact that chlorplatinic acid gave no precipitate with a solution of the substance.

Properties. — The trichloride of pentamidobenzol, as precipitated by hydrochloric acid from its aqueous solution, is seen under the microscope to consist of rather thick well developed transparent rhombic plates, with the sharper angles truncated by a single plane. It is colorless when first prepared, but soon turns pink or gray, and on long standing passes through dark brown to black, a change which is much accelerated by heat; yet even after it has become nearly black, if examined with the microscope, it is found to retain unaltered its crystalline form, and the individual crystals are still transparent, although very much darkened, so that this change in color seems to have taken place only superficially. It is very easily soluble in water, but only slightly soluble in strong hydrochloric acid, a property which is useful in the purification of the substance. The aqueous solution decomposes quickly when heated, a black tar being formed, and a similar change takes place more slowly at ordinary temperatures, the solution becoming at first clear pink, and then darkening through shades of red to black. The action of more violent oxidizing agents is described below, and resembles that of the air. The salt when dry or moistened with strong hydrochloric acid is much more stable than a solution, or the wet salt. The substance is sparingly soluble in alcohol and essentially insoluble in ether, benzol, or chloroform.

If ammonic hydrate is added with caution to a concentrated solution of the salt, a black jelly is precipitated; if the solution is dilute, no precipitate is formed, but the liquid takes on a pink color, which in a few minutes passes through purple and violet blue to a yellowish green; from this solution hydrochloric acid precipitates black flocks, which redissolve in an excess of the acid, or on the addition of ammonic hydrate. Sodic hydrate acts on the chloride in the same way. The free base seems to be insoluble in ether; at any rate, nothing was extracted by this solvent from an aqueous solution of the salt, to which an excess of sodic hydrate had been added. It is evident from the observations just described, that the isolation of the free base would be a matter of great difficulty.

The foregoing results correspond to those of Barr in every respect except the crystalline form of the chloride, which he describes as white needles as fine as hairs. He also made the pentacetyl compound $C_6H(NHC_2H_3O)_5$.

Chlorplatinic acid with a solution of the trichloride of pentamidobenzol gives no precipitate at first, but after some time a slimy brown substance is deposited on the sides of the test-tube, evidently a product of oxidation. We are inclined to think, however, that the oxidizing agent is the oxygen of the air rather than the chlorplatinic acid, as a similar result was obtained by the action of picric acid. Benzaldehyd added to a solution of the salt also gave a tarry product.

When the trichloride of pentamidobenzol is treated with nitric acid and ferric chloride, a deep purple solution* is formed looking very much like potassic permanganate, and when an excess of the ferric chloride has been added, a brown flocculent precipitate is deposited, which when dried forms a hard mass of a brown color without crystalline form, since under the microscope it appears to be made up of sandy granules. It is slightly soluble in water, imparting to it a dark brown color. Preliminary analyses gave the following results.

0.1600 grm. of the substance on combustion gave 0.2592 grm. of carbonic dioxide and 0.0650 grm. of water.

0.1685 grm. of the substance gave according to the method of Carius 0.0797 grm. of argentic chloride.

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* Compare this with the action of air on a solution of the salt or of the free base described earlier in this paper.

	Found.
Carbon	44.18
Hydrogen	4.51
Chlorine	11.69

We were engaged on the study of this substance when we received Barr's paper, and accordingly stopped our work on this subject, and we publish these analyses only because they may be of use to any one who may continue the investigation of this substance, as it would be idle to try to derive a formula from them until they have been supported by further work. Barr also observed the formation of this substance, but did not attempt to study it carefully, or analyze it.

It seems probable that the pentamidobenzol, in addition to the trichloride, can form a *pentachloride*, as one of our first preparations, in which the reduction was carried on at a lower temperature than usual, yielded a substance which, dried at first in a desiccator over calcic chloride without any alkaline absorbent, and finally for a short time in an air bath at 90°, gave the following result on analysis.

0.1738 grm. of the substance gave 30.9 c.c. of nitrogen at a temperature of 6° and a pressure of 750 mm.

	Calculated for $C_6H(NH_3Cl)_5$.	Found.
Nitrogen	20.86	21.37

The appearance of Barr's paper has prevented us from making another attempt to prepare this substance. If it is a definite compound, it is a very unstable one, as it gave off a distinct smell of hydrochloric acid.

Trianilidodinitrobenzol, $C_6H(C_6H_5NH)_3(NO_2)_2$.

This substance can be made by heating for a short time aniline with tribromdinitrobenzol in the proportion of six molecules of the base to one of the bromine compound. It seems that the two substances do not act on each other in the cold, or, if there is any action, it is a very slow one, and in this respect the dinitro compound differs from the tribromtrinitrobenzol, which acts on aniline quickly at ordinary temperatures. The product was purified by crystallizing it from alcohol till it showed the melting point 179°, dried at 100°, and analyzed with the following results.

I. 0.1820 grm. of the substance gave on combustion 0.4347 grm. of carbonic dioxide and 0.0760 grm. of water.

II. 0.1906 grm. of the substance gave 26 c.c. of nitrogen at a temperature of 12° and a pressure of 762 mm.

III. 0.1815 gr. of the substance gave 26 c.c. of nitrogen at a temperature of 17° and a pressure of 743 mm.

	Calculated for	Found.		
	$C_6H(NHC_6H_5)_3(NO_2)_2$.	I.	II.	III.
Carbon	65.31	65.13		
Hydrogen	4.30	4.64		
Nitrogen	15.88		16.24	16.24

Properties. — The trianilidodinitrobenzol, when crystallized from alcohol, forms vivid orange-red needles, which under the microscope appear as long prisms terminated by a single plane at angles not very far from right angles to the sides, occasionally groups of radiating needles are observed also. When crystallized from ether, it forms irregularly spherical crowded groups of short stout radiating prisms with blunt ends made up of several planes, a form which is decidedly characteristic. It melts at 179°, and is essentially insoluble in either cold or boiling water, or in ligroine; slightly soluble in cold alcohol, freely in hot; moderately soluble in ether, carbonic disulphide, glacial acetic acid, or acetone; freely soluble in benzol, or chloroform, but the substance is deposited from the two solvents last mentioned in an amorphous form, so that hot alcohol is the best solvent for it. Strong hydrochloric acid, either hot or cold, has no perceptible action on it. Strong nitric acid dissolves a very little, with a pale yellow color; strong sulphuric acid dissolves rather more of the substance, with a stronger yellow color. Upon heating it with either of these last two acids it is charred. It is therefore, as was to be expected, less basic in its properties than the triamidodinitrobenzol.